Project Number: **86740**
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Project Title: Phosphate Barriers for Immobilization of Uranium Plumes

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Number of Graduate Students Involved: 2

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RESEARCH OBJECTIVES

Uranium contamination of the subsurface remains a persistent problem plaguing remedial design at sites across the U.S. that were involved with production, handling, storage, milling, and reprocessing of uranium for both civilian and defense related purposes. Remediation efforts to date have relied upon excavation, pump-and-treat, or passive remediation barriers (PRB's) to remove or attenuate uranium mobility. Documented cases convincingly demonstrate that excavation and pump-and-treat methods are ineffective for a number of highly contaminated sites. There is growing concern that use of conventional PRB's, such as zero-valent iron, may be a temporary solution to a problem that will persist for thousands of years. Alternatives to the standard treatment methods are therefore warranted. The core objective of our research is to demonstrate that a phosphorous amendment strategy will result in a reduction of dissolved uranium to below the proposed drinking water standard. Our hypothesis is that long-chain sodium polyphosphate compounds forestall precipitation of sparingly soluble uranyl phosphate compounds, which is paramount to preventing fouling of wells at the point of injection.

RESEARCH PROGRESS AND IMPLICATIONS

This report summarizes the third year of progress in the three-year project. Hydraulically saturated and unsaturated column tests demonstrate the ability of sodium polyphosphate compounds to control the precipitation kinetics of sparingly soluble phosphate minerals and optimize conditions for controlled application of phosphate amendments for subsurface remediation. X-Ray micro-focus tomography (XMT) results illustrate long-term effects of phosphate mineralization on hydraulic conductivity. ^{31}P NMR was utilized to quantify the effect of sedimentary and aqueous components on the *in-situ* hydrolysis kinetics of condensed polyphosphates. Single-pass flow-through (SPFT) tests were conducted to evaluate the dissolution kinetics of autunite minerals. Solution drop calorimetry established the thermodynamic properties of autunite minerals. Results indicate: (1) autunite minerals will precipitate within 1-2 months given a 0.05 M phosphate concentration and 10^{-6} M aqueous uranium concentration, under hydraulically saturated conditions; (2) direct comparison between previously proposed phosphate remediation solutions, phytic acid, trisodium (mono)phosphate (TSP) and sodium citrate, versus our proposed sodium polyphosphate amendment solution, shows that the phytic acid and TSP solutions cause plugging of the column due to rapid precipitation of phosphate minerals, whereas the sodium polyphosphate solution did not cause precipitation for up to 2 months, thus keeping the hydraulic conductivity of the column intact (Table 1); (3) polyphosphate chain lengths can be optimized for specific site conditions, given

knowledge of the subsurface environment; (4) the release of uranium from autunite minerals is 6-7 orders of magnitude slower than release from uranium minerals (UO_2) formed by, e.g., iron barrier reduction; and (5) free energy values firmly established the extremely low solubility of autunite. Our findings persuasively demonstrate that employment of polyphosphate amendment solutions will effectively immobilize subsurface uranium plumes without causing an immediate reduction in hydraulic conductivity.

Table 1. Hydraulic conductivity data for column tests with Hanford soil saturated with calcite equilibrated solution (pH=8). The data indicate significant reduction in hydraulic conductivity with addition of phytic acid, trisodium (mono)phosphate (TSP), and sodium citrate, but not with the sodium polyphosphate.

	Phytic Acid	Monophosphate $Na_3(PO_4)(H_2O)_{12}$	Na Polyphosphate $[Na_3(PO_4)]_n$	Sodium Citrate
Average Hydraulic Conductivity (before phosphate treatment)	0.37	0.61	0.28	0.34
Average Hydraulic Conductivity (after phosphate treatment)	0.26	0.45	0.29	4.37×10^{-4}
% Difference:	-29.73 (±5)	-26.23 (±5)	+3.57 (±5)	-99.87(±5)

INFORMATION ACCESS

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